

SUPPLEMENTARY INFORMATION

Molecular Structure and Thermal Stability of Oxide-
Supported Phosphotungstic Wells-Dawson Heteropolyacid

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X-ray Diffraction Analysis

The X-ray diffraction spectra of the bulk phosphotungstic heteropolyacid $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot x\text{H}_2\text{O}$, the oxide supports and the samples 11aq WDTi, 11aq WDZr, 12aq WDAI and 11aq WDSi (calcined at 573 K for 4 h) were performed at RT with a D5000 diffractometer (Siemens, Germany) with Ni filter, Cu K α ($\lambda=1.540589$ Å) radiation working at 40 kV and 20 mA. The diffraction patterns were obtained within $2\theta=5^\circ$ and 60° at a scan rate of 2° min^{-1} and steps of 0.1° . The following figure shows the X-ray spectra of the bulk HPA, the bare oxide supports and the supported HPA synthesized in aqueous media.

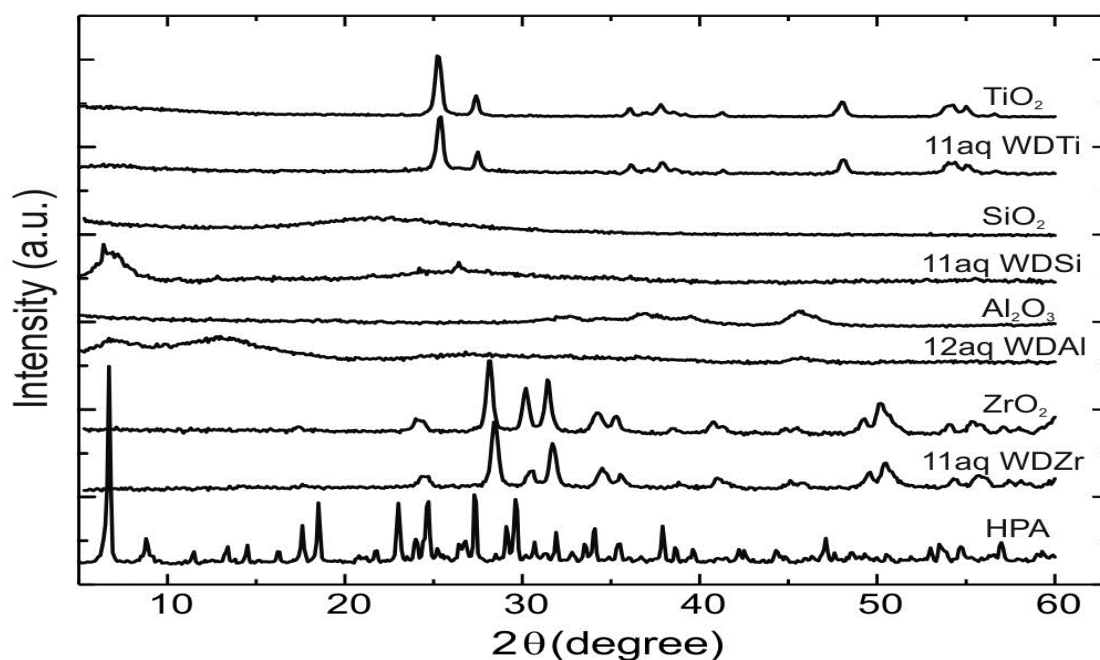


Figure 1S. X-Ray diffraction spectra of bulk phosphotungstic Wells-Dawson heteropolyacid $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 24\text{H}_2\text{O}$; bare oxide supports (SiO_2 , TiO_2 , Al_2O_3 and ZrO_2) and oxide-supported HPA (11aq WDTi, 11aq WDSi, 12aq WDAI and 11aq WDZr)

Temperature Programmed Raman Spectra of Transition Metal Oxide Supports

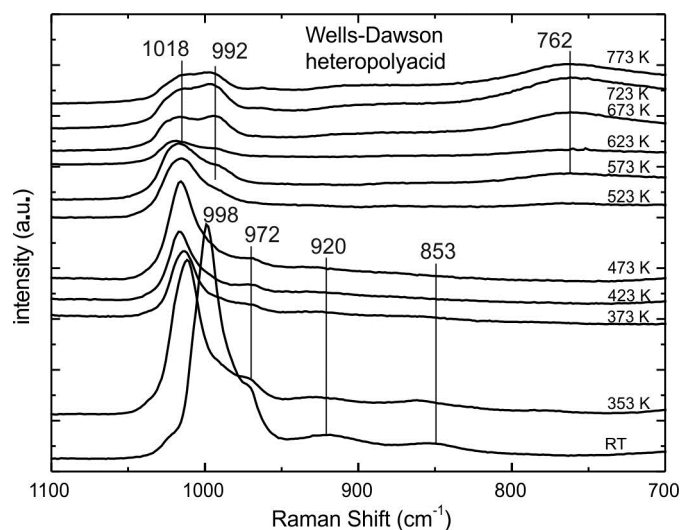


Figure 2S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of bulk phosphotungstic Wells-Dawson heteropolyacid $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot x\text{H}_2\text{O}$

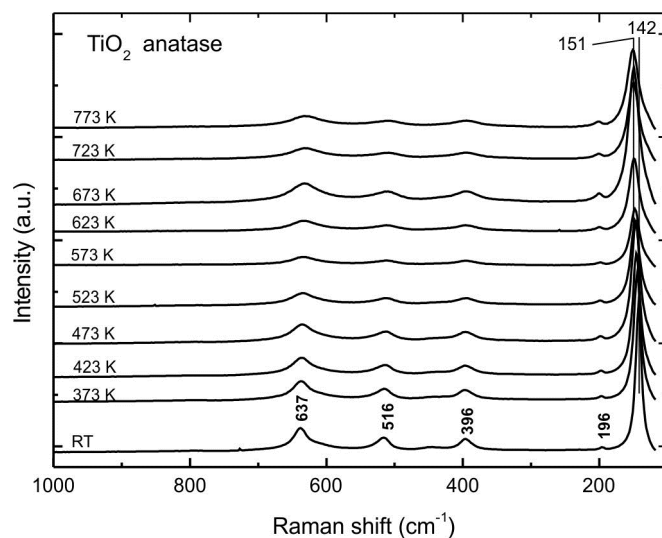


Figure 3S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of titanium dioxide TiO_2 anatase (Aeroxide® P-18 Evonik Ind., $46.8 \pm 0.1 \text{ m}^2/\text{g}$)

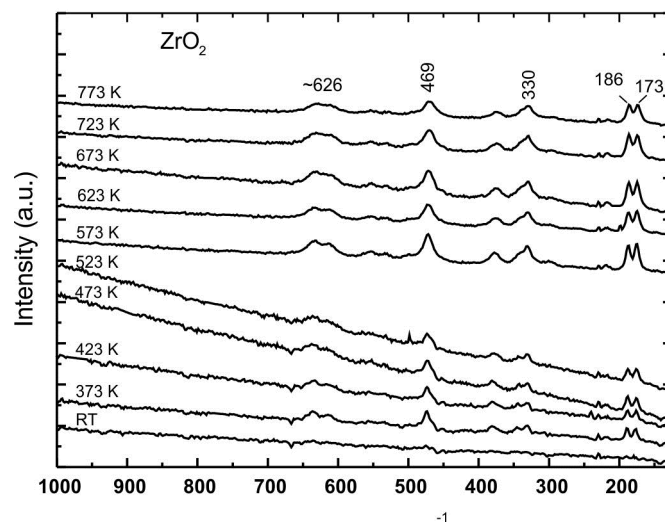


Figure 4S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of zirconium dioxide ZrO_2 (fumed Evonik Ind., $31.5 \pm 0.4 \text{ m}^2/\text{g}$)

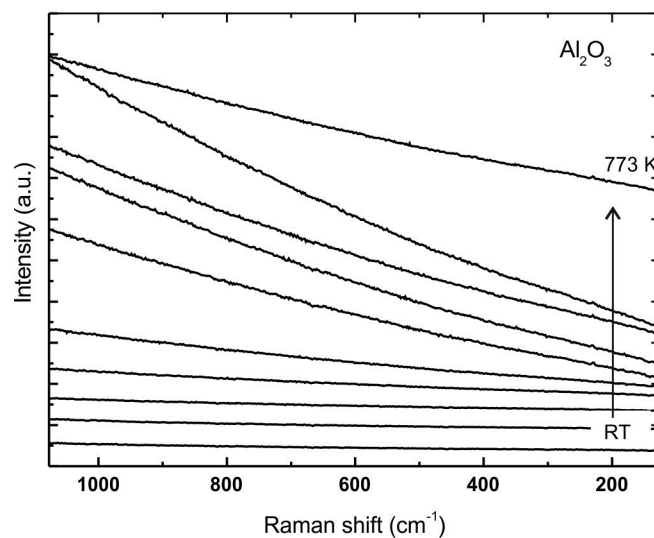


Figure 5S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of alumina Al_2O_3 (Engelhard, $95.8 \pm 0.2 \text{ m}^2/\text{g}$)

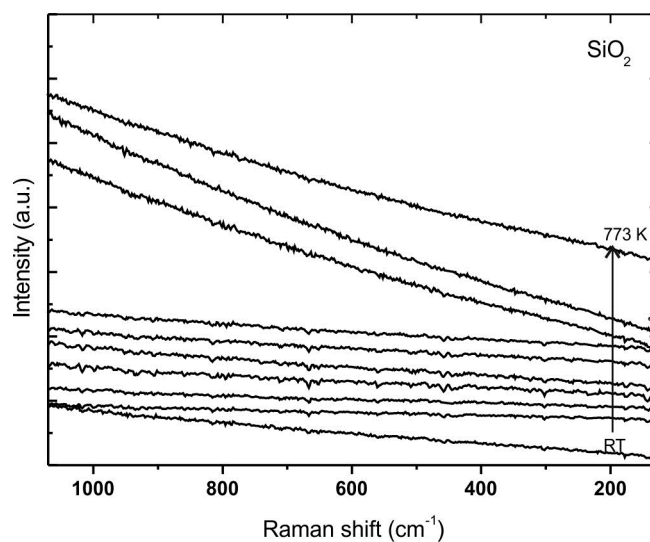


Figure 6S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of silica SiO₂ (Cab-O-Sil, 328.9 ± 0.8 m²/g)

Temperature Programmed Raman Spectra of Oxide-supported Wells-Dawson Heteropolyacid Synthesized in Organic Media

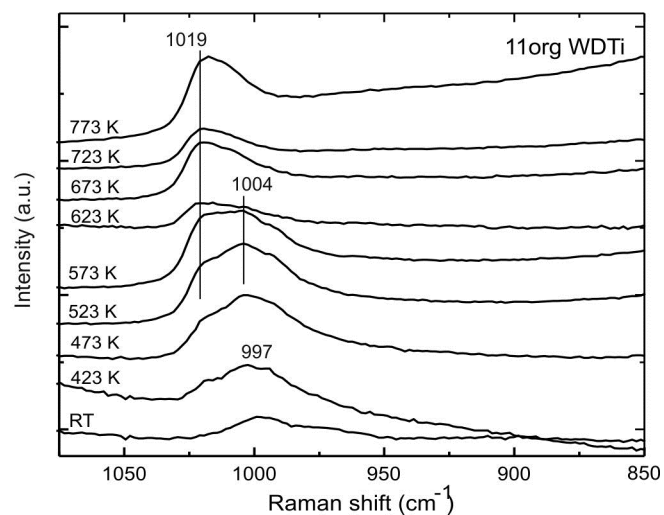


Figure 7S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of 11org WDTi

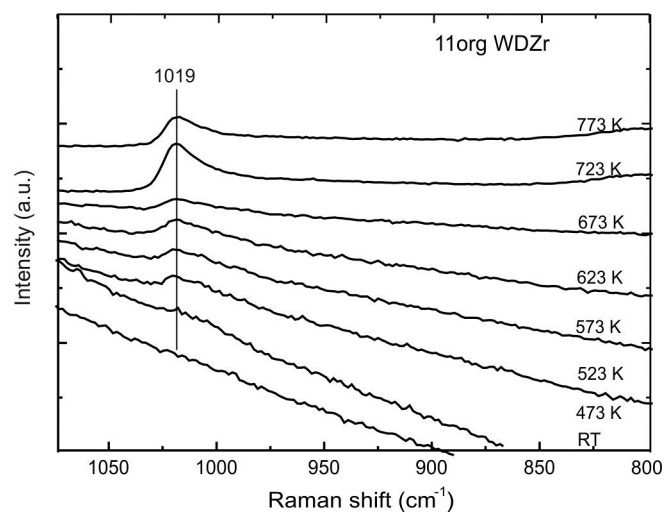


Figure 8S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of 11org WDZr

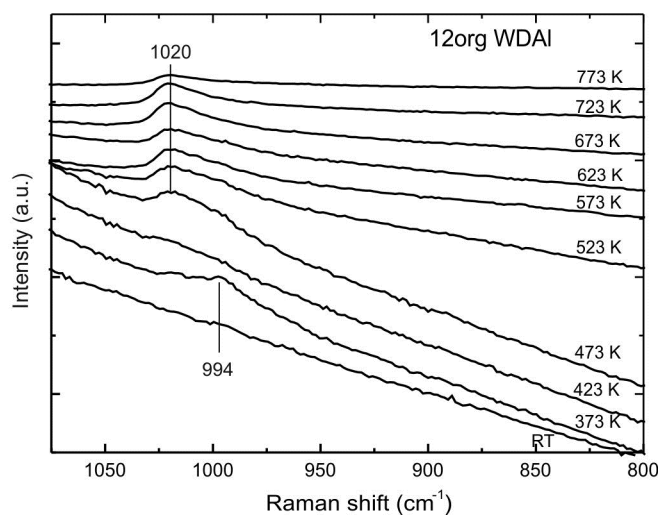


Figure 9S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of 12org WDAI

Temperature Programmed Infrared Spectra of Transition Metal Oxide Supports

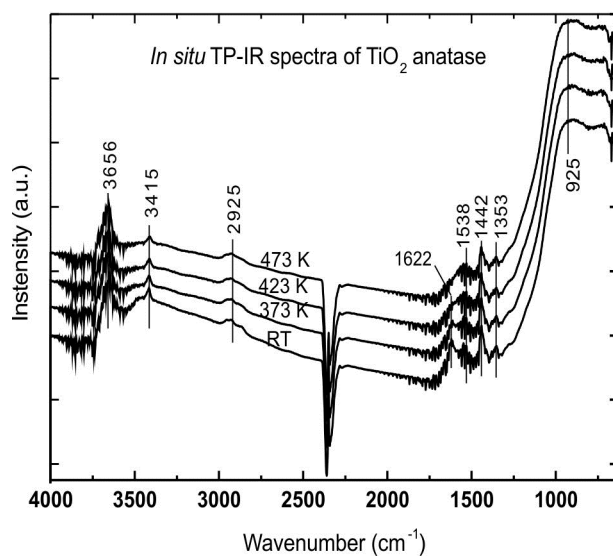


Figure 10S. *In situ* TP-IR spectra upon heating from R.T. towards 773 K of titanium dioxide TiO₂ anatase (Aeroxide® P-18 Evonik Ind., 46.8 ± 0.1 m²/g).

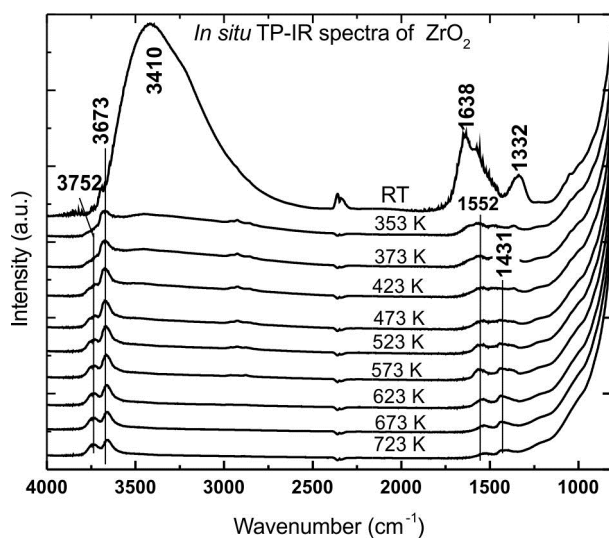


Figure 11S. *In situ* TP-IR spectra upon heating from R.T. towards 773 K of zirconium dioxide ZrO₂ (fumed Evonik Ind., 31.5 ± 0.4 m²/g).

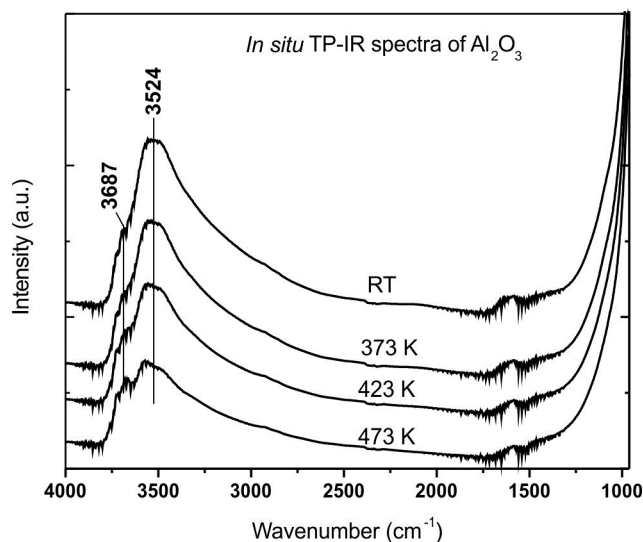


Figure 12S. *In situ* TP-IR spectra upon heating from R.T. towards 773 K of alumina Al_2O_3 (Engelhard, $95.8 \pm 0.2 \text{ m}^2/\text{g}$).

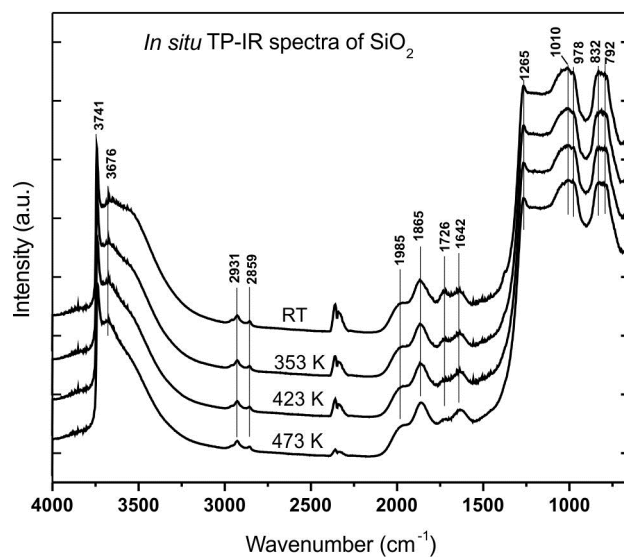


Figure 13S. *In situ* TP-IR spectra upon heating from R.T. towards 773 K of silica SiO_2 (Cab-O-Sil, $328.9 \pm 0.8 \text{ m}^2/\text{g}$).

Evolution of the Raman Signals of the Wells-Dawson Heteropolyacid Dispersed
Over TiO_2 at Various Loadings

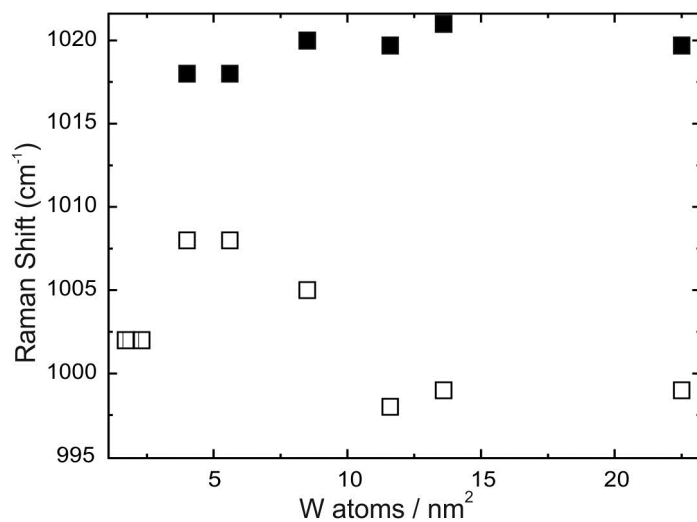


Figure 14S. Evolution of the Raman signals of the Wells-Dawson heteropolyacid dispersed over TiO_2 at various loadings ranging from 1.7 towards 22.5 $W_{\text{atoms}}/\text{nm}^2$ in aqueous media and calcined *in situ* at 573 K. Open squares \square indicate Raman signals in the 999-1008 cm^{-1} range and filled squares \blacksquare indicate Raman signals in the 1018-1021 cm^{-1} range